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Report Title

Final Report on Patterning and Fabrication of Conductive Nanowires as Interconnects for Nanoelectronic Circuits Using Nucleic Acid Molecules as Templates

ABSTRACT

We studied the construction of nanometer-dimension materials from aligned DNA on surfaces. We devised an approach for synthesizing DNA-templated copper nanowires on substrates; these nanostructures have diameters as large as ~10 nm and lengths greater than 10 micrometers. We also developed a facile method for reducing nonspecific surface metallization for DNA-templated nanowires; this technique was applied in creating silver nanowires from single-stranded DNA. We further designed substrates with unique spatial addressing to allow the measurement of surface features repeatedly using complementary microscopic techniques (e.g., atomic force and electron microscopy). In addition, we demonstrated the localization of carbon nanotubes onto aligned surface DNA, by using 1-pyrenemethylamine as a bridging compound to facilitate nanotube assembly. Moreover, we devised and evaluated a gas flow cell system for making aligned carbon nanotube arrays on surfaces. We improved upon our initial DNA-nanotube deposition approach by localizing surfactant-wrapped nanotubes onto surface-aligned DNA with a coverage >80%. Furthermore, we evaluated self-assembling, three-branched DNA nanostructures as three-terminal nanodevice templates; characterized the metallization of these assemblies; and studied the specific localization of nanostructures within these complexes. Lastly, we made and characterized DNA-templated nickel nanowires. Our success in DNA-templated nanowire fabrication should facilitate future developments in nanoelectronics.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Monson, C.F.; Woolley, A.T. DNA-Templated Construction of Copper Nanowires. Nano Lett. 3, 359-363 (2003).

Xin, H.; Woolley, A.T. DNA-Templated Nanotube Localization. J. Am. Chem. Soc. 125, 8710-8711 (2003).

Becerril, H.A.; Stoltenberg, R.M.; Monson, C.F.; Woolley, A.T. Ionic Surface Masking for Low Background in Single- and Double-Stranded DNA-Templated Silver and Copper Nanorods. J. Mater. Chem. 14, 611-616 (2004).

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Xin. H.; Woolley, A.T. High-Yield DNA-Templated Assembly of Surfactant-Wrapped Carbon Nanotubes. Nanotechnology 16, 2238-2241 (2005).

Number of Papers published in peer-reviewed journals: 7.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Woolley, A.T. Biofunctionalization of Carbon Nanotubes for Atomic Force Microscopy Imaging. Meth. Mol. Biol. 283, 305-319 (2004).

Becerril, H.A.; Nelson, A.R.; Woolley, A.T. Micromachined Substrates for Molecular Follow-Up in DNA-Templated Nanofabrication. AIP Conf. Proc. 725, 31-40 (2004).

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Woolley, A.T.; Hughes, S.D.; Monson, C.F.; Nelson, A.R.; Xin, H.; Craw J.R. DNA Alignment, Characterization and Nanofabrication on Surfaces. Presented at the BioMEMS and Biomedical Nanotechnology World 2002 Conference. Columbus, OH, September, 2002 (invited talk).

Woolley, A.T.; Hughes, S.D.; Monson, C.F.; Nelson, A.R.; Xin, H.; Craw, J.R.; Becerril-Garcia, H.A. DNA-templated nanofabrication and nanopositioning on surfaces. Presented at the 225th ACS National Meeting, Industrial and Engineering Chemistry Division, New Orleans, LA, March 2003; paper 217 (invited talk).

Woolley, A.T. Miniaturization in Biochemical Analysis: From Microfluidics to Nanotechnology and Beyond. Presented at the 2003 Analytical Chemistry Gordon Research Conference, New London, CT, June 2003 (invited talk: young investigators session).

Woolley, A.T.; Hughes, S.D.; Monson, C.F.; Nelson, A.R.; Xin, H.; Craw, J.R.; Becerril, H.A. Surface Aligned DNA for Nanofabrication and Genetic Analysis. Presented at the BioMEMS and Biomedical Nanotechnology World 2003 Conference, Washington, DC, August, 2003 (poster).

Woolley, A.T. DNA-templated nanofabrication: integration of synthetic nanotechnology with biology. Presented at the US-Japan Symposium on Nanotechnology in Advanced Therapy and Diagnosis, Yokohama, Japan, October, 2003 (invited talk).

Becerril, H.A.; Stoltenberg, R.M.; Woolley, A.T. Ionic masking for low-background metallization of single-stranded DNA. Presented at the 227th ACS National Meeting, Analytical Chemistry Division, Anaheim, CA, March 2004 (poster).

Stoltenberg, R.M.; Becerril, H.A.; Monson, C.F.; Woolley, A.T. DNA-templated fabrication of copper nanowires. Presented at the 227th ACS National Meeting, Analytical Chemistry Division, Anaheim, CA, March 2004 (poster).

Woolley, A.T. DNA-Templated Fabrication of Nanostructures for Bottom-Up Nanoelectronic Systems, Army Research Office Workshop for the On-Chip Detection of Biological and Chemical Molecules, Raleigh, NC, April 2004 (invited talk).

Woolley, A.T. DNA-Templated Fabrication of Carbon Nanotube and Metal Nanowires. International Symposium on DNA-Based Molecular Electronics, Jena, Germany, May 2004 (invited talk).

Becerril-Garcia, H.A.; Harrison, R.G.; Woolley, A.T. Advances in DNA-Templated Nanofabrication of Electronic Devices. Presented at the Joint ACS 59th Northwest and 18th Rocky Mountain Regional Meeting, Logan, UT, June 2004; paper 208 (poster).

Xin, H.; Woolley, A.T. Controlled Orientation of Single-Walled Carbon Nanotubes on Surfaces. Presented at the Joint ACS 59th Northwest and 18th Rocky Mountain Regional Meeting, Logan, UT, June 2004; paper 209 (poster).

Woolley, A.T. DNA-Templated Three-Branched Nanostructures. Society of Western Analytical Professors (SWAP) 2005, Fort Collins, CO, January, 2005 (contributed talk).

Woolley, A.T. DNA-Templated Linear and Three-Branched Nanostructures. Research Seminar at Cambrios Technologies, Mountain View, CA, March 22, 2005.

Xin, H.; Woolley, A. T. DNA-Templated Nanotube Arrays. Presented at the 230th ACS National Meeting, Inorganic Chemistry Division, Washington, D.C., August 2005; paper 413 (poster).

Number of Papers not Published: 14.00

(d) Manuscripts

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Number of Inventions:

Graduate Students

NAME	PERCENT_SUPPORTED	
Hector A. Becerril	1.00	No
Allison R. Nelson	1.00	No
Huijun Xin	1.00	No
FTE Equivalent:	**3.00**	
Total Number:	**3**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Adam T. Woolley	0.17	No
FTE Equivalent:	**0.17**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED	
Christopher F. Monson	0.50	No
Randall M. Stoltenberg	0.50	No
FTE Equivalent:	**1.00**	
Total Number:	**2**	

Names of Personnel receiving masters degrees

NAME	
Allison R. Nelson	No
Total Number:	**1**

Names of personnel receiving PHDs

NAME
Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Final Progress Report

U.S. Army Research Office

DAAD19-02-1-0353

by Adam T. Woolley

Abstract

We studied the construction of nanometer-dimension materials from aligned DNA on surfaces. We devised an approach for synthesizing DNA-templated copper nanowires on substrates; these nanostructures have diameters as large as ~10 nm and lengths greater than 10 micrometers. We also developed a facile method for reducing nonspecific surface metallization for DNA-templated nanowires; this technique was applied in creating silver nanowires from single-stranded DNA. We further designed substrates with unique spatial addressing to allow the measurement of surface features repeatedly using complementary microscopic techniques (e.g., atomic force and electron microscopy). In addition, we demonstrated the localization of carbon nanotubes onto aligned surface DNA, by using 1-pyrenemethylamine as a bridging compound to facilitate nanotube assembly. Moreover, we devised and evaluated a gas flow cell system for making aligned carbon nanotube arrays on surfaces. We improved upon our initial DNA-nanotube deposition approach by localizing surfactant-wrapped nanotubes onto surface-aligned DNA with a coverage >80%. Furthermore, we evaluated self-assembling, three-branched DNA nanostructures as three-terminal nanodevice templates; characterized the metallization of these assemblies; and studied the specific localization of nanostructures within these complexes. Lastly, we made and characterized DNA-templated nickel nanowires. Our success in DNA-templated nanowire fabrication should facilitate future developments in nanoelectronics.

List of illustrations

Statement of the problem studied. We tested the hypothesis that specific localization and orientation of DNA fragments on surfaces, followed by assembly of conductive material along the nucleic acid templates, would constitute DNA-based nanolithography, which would allow the creation of nanowires for electrical connections in integrated circuits. Furthermore, we studied whether the sequence of deposited DNA could serve as a scaffold for controlled positioning of nanostructures coupled to oligonucleotides, through specific hybridization to their complementary sequence on the surface template. We were successful in carrying out experiments that confirm our hypothesis. The results are detailed in the following pages.

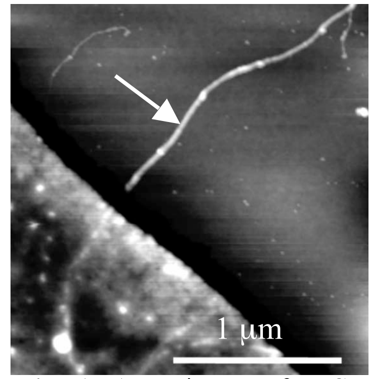

Fig. 1. AFM image of a Cu nanowire (arrow) at the interface between SiO_2 (right) and a gold microelectrode (left). Height scale is 20 nm.

Summary of the most important results. We developed methods for the construction of copper nanowire structures on surfaces from DNA templates. Cu(II) ions were associated with the negatively charged DNA backbone and were reduced to copper metal using ascorbic acid. Multiple treatment steps allowed for the construction of nanowires having heights of several nanometers, corresponding to 5-10 Cu atom thicknesses.[1] We then made significant improvements to our initial approach for the fabrication of DNA-templated copper nanowires. This work enabled the growth of much longer copper nanowires (initial experiments: hundreds of nanometers; optimized approach: nearly 10 microns) and larger-diameter nanowires (initial studies: ~3 nm; optimized method: ~10 nm), as illustrated in Fig. 1. Much of this improvement was achieved by exchanging the copper ions with DNA in a solvent (DMSO) with a lower dielectric constant than water to enhance DNA-copper ion interaction.[2]

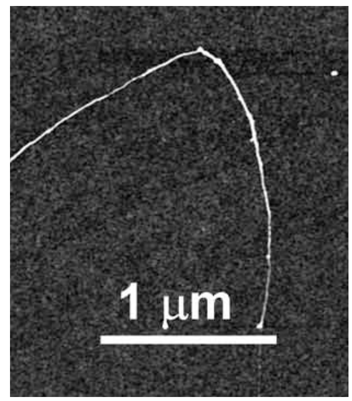

Fig. 2. AFM height image of a low-background dsDNA-templated Cu nanowire fabricated using K^+ as a masking ion.

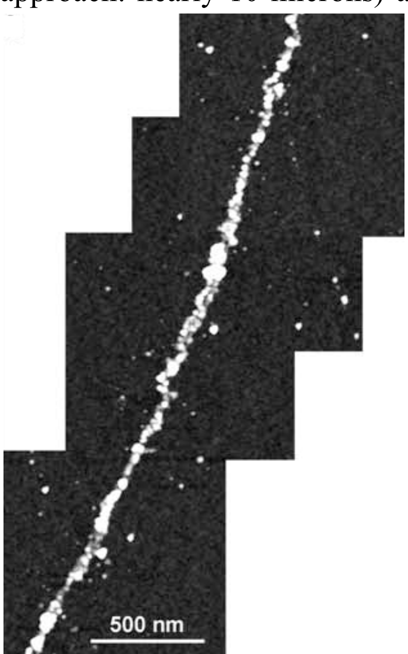

Fig. 3. AFM height image of a low-background ssDNA-templated Ag nanowire.

We also developed an approach for reducing the nonspecific background that occurred during metallization of surface DNA. We demonstrated that potassium and cesium ions effectively block the nonspecific adsorption of copper(II) and silver(I) cations on silicon surfaces, leading to a several-fold decrease in the quantity and size of randomly deposited surface metal particles surrounding DNA-templated metallic nanostructures (Fig. 2).[3] We further showed for the first time that single-stranded DNA deposited on surfaces could be metallized to form nanowires, as illustrated in Fig. 3. Indeed, we generated silver nanowires from single-stranded lambda DNA on surfaces and characterized the morphology of the resulting nanostructures.[3]

To facilitate the characterization of surface DNA-templated nanostructures, we produced micromachined silicon substrates with unique spatial addressing for surface-aligned DNA molecules. Repeated assessment of the same molecule using atomic force microscopy and/or scanning electron microscopy before and after nanofabrication treatments was achieved. Utilizing these micromachined platforms as substrates in nanofabrication experiments enabled the use of complementary microscopy techniques for data collection on selected features of interest at different stages of a nanofabrication process. In this way, a clear correlation of the information generated was achieved.[4]

Moreover, we studied the use of DNA as a template for the alignment and positioning of carbon nanotubes on surfaces. We found that 1-pyrenemethylamine (PMA) facilitated the localization of multi-walled and single-walled carbon nanotubes (SWNTs) onto DNA molecules aligned on substrates. Indeed, ~60% of all surface-adsorbed nanotubes were aligned on PMA-treated DNA, although the overall coverage of the surface DNA with nanotubes was about 5% (see Fig. 4).[5] We also devised a simple procedure for the alignment of SWNTs with controlled orientation on surfaces from a droplet of nanotube suspension under gas flow.[6] With this method we found that ~85% of nanotubes were aligned to within ±10 degrees of the direction of gas flow. Orthogonally arranged arrays of SWNTs were also fabricated in a two-step process. Studies of fluid motion within droplets in the flow cell indicated that alignment was likely due to the circulation of SWNTs in the suspension droplet.[6] The gas flow alignment method provided a facile system for generating oriented nanotubes on surfaces, and this approach could find use in SWNT nanodevice fabrication.

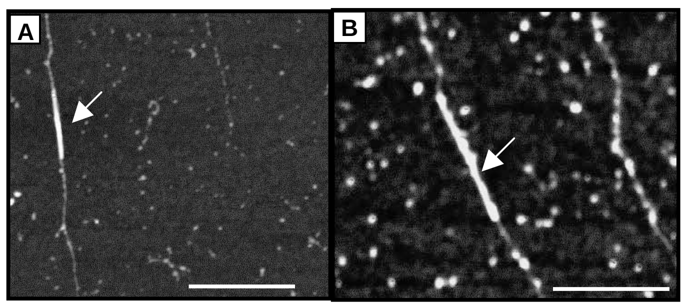

Fig. 4. AFM height images of two different substrates where SWNTs were deposited onto PMA-treated λ DNA. White arrows indicate SWNTs. The height scale is 18 nm and the white bar indicates 500 nm in (A), while the height scale is 4 nm and the white bar indicates 250 nm in (B).

We also developed a straightforward technique for constructing SWNT assemblies by using aligned surface DNA as a positioning template.[7] A cationic surfactant, dodecyltrimethylammonium bromide (DTAB), was utilized to suspend SWNTs in aqueous media and localize them on DNA through electrostatic interactions. SWNT positioning was controlled by the surface DNA arrangement, and the extent of deposition was influenced by the SWNT concentration (see Fig. 5). With lower concentration SWNT suspensions, multiple surface treatments increased the DNA coverage. Under optimized condi-

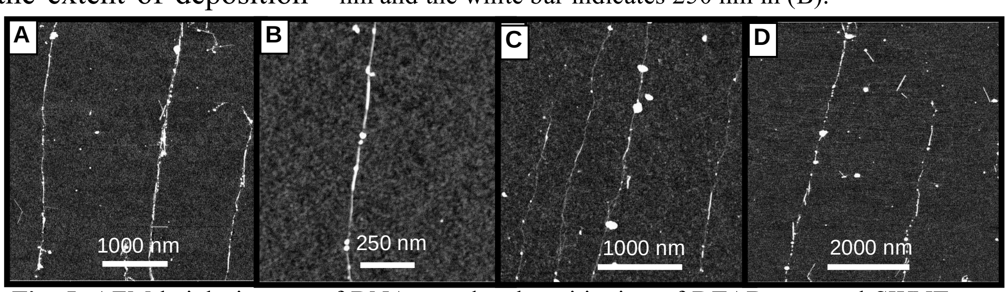

Fig. 5. AFM height images of DNA-templated positioning of DTAB-wrapped SWNTs on Si surfaces. (A) Large-area image of a DNA surface treated for 10 min with a 1% DTAB suspension of ~0.1 mg/mL SWNTs. (B) Smaller-area image of the surface in (A). (C) Image of a surface treated for 10 min with a 1% DTAB suspension of ~0.02 mg/mL SWNTs. (D) AFM image of the surface in (C) after three treatments for 10 min with a 1% DTAB suspension of ~0.02 mg/mL SWNTs. Height scale is 5 nm in all images.

tions, 83% of the length of surface DNA was covered with SWNTs, and 76% of all surface-deposited SWNTs were on the DNA. In some regions, nearly continuous SWNT assemblies were formed.[7] This approach should provide a useful tool for the fabrication of nanotube nanowires in nanoelectronic circuits.

Three-branched DNA molecules were designed and assembled from oligonucleotide components (Fig. 6).[8] These nucleic acid constructs contained double- and single-stranded regions that controlled the hybridization behavior of the assembly. Specific localization of a single streptavidin molecule at the center of the DNA complex was investigated as a model system for the directed placement of nanostructures (Fig. 7). Highly selective silver and copper metallization of the DNA template was also characterized (Fig. 8).[8] Specific hybridization of these DNA complexes to oligonucleotide-coupled nanostructures, followed by metallization, should provide a bottom-up self-assembly route for the fabrication and characterization of discrete three-terminal nanodevices.

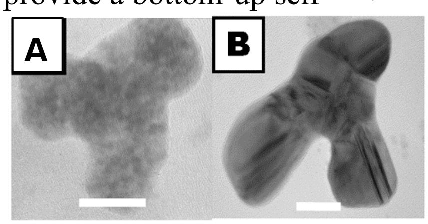

Fig. 8. TEM images of DNA-templated metallization of three-armed complexes with (A) copper or (B) silver; scale bars are 25 nm.

Finally, we constructed nickel nanowires from aligned surface DNA. A droplet of a saturated ethanolic solution of $Ni(NO_3)_2$ was placed on a substrate having elongated DNA, and reduction to nickel metal was accomplished in an ethanolic solution of oxalic acid. Atomic force microscopy images (Fig. 9A) demonstrated that nickel treatment and reduction led to an increase in feature height specific to the aligned surface DNA. Moreover, scanning transmission electron microscopy (STEM, Fig. 9B) and energy-dispersive X-ray analysis (EDX, Fig. 9C) further corroborated that this approach led to DNA-specific assembly of nickel.

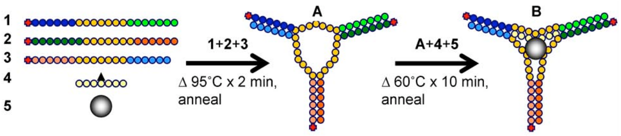

Fig. 6. (1-3) ~120 base oligonucleotides with complementary regions represented as tonal variations of the same color (i.e. dark vs. light green). (4) Internally biotinylated poly-T sequence, complementary to the dark yellow regions in (1-3). (5) Streptavidin. (A) Three-branched DNA nanostructure assembly. (B) Streptavidin-labeled, three-armed DNA complex.

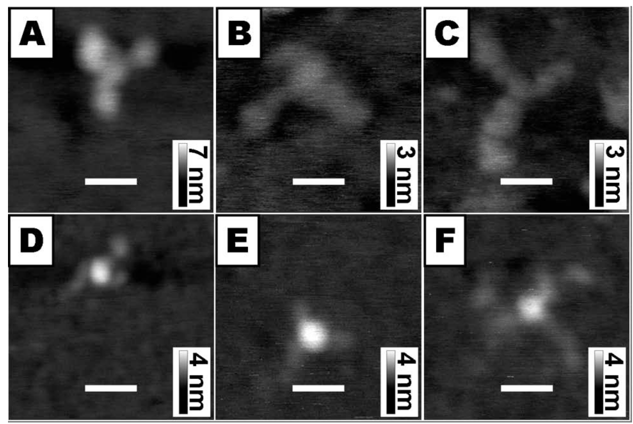

Fig. 7. Tapping-mode AFM height images of mica surfaces with three-branched DNA structures (A-C) and complexes with streptavidin localized in the center (D-F). The white bar represents 25 nm in all images.

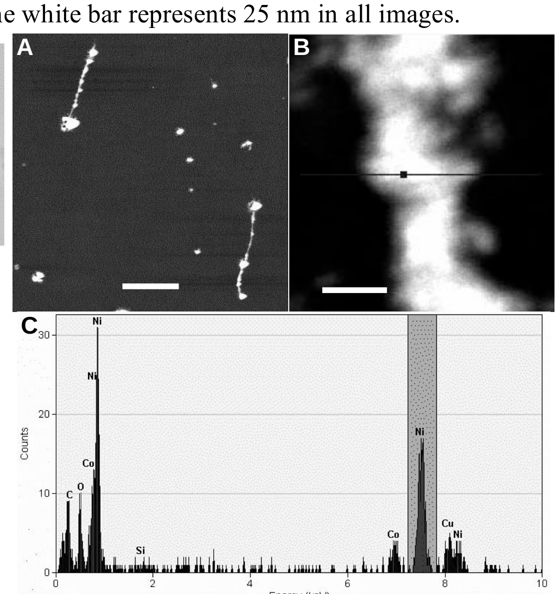

Fig. 9. Characterization of DNA-templated fabrication of Ni nanowires. (A) AFM height image; scale bar is 1000 nm and height scale is 15 nm. (B) STEM image; scale bar is 20 nm. (C) EDX spectrum for the position marked by the square on the horizontal line in (B); Ni is the principal component.

Conclusions. The continued push to make faster and better integrated circuits will necessitate further miniaturization of their constituent components. While minor modifications to present methods offer the possibility to achieve incremental reductions in feature size, albeit with increased cost, the development of new, perhaps unconventional approaches for making nanometer-scale integrated circuits is an attractive alternative. Here, we have determined that the specific localization and orientation of DNA fragments on surfaces, followed by assembly of conductive material along the nucleic acid templates, constitutes DNA-based nanolithography, which allows the creation of nanowires for potential electrical connections in integrated circuits. We have also found that the sequence of deposited DNA can serve as a scaffold for the controlled positioning of nanostructures coupled to oligonucleotides, through specific hybridization to their complementary sequence on the surface template. These advances offer considerable potential in the downscaling of nanowires for future nanoelectronics applications.

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1. Monson, C.F.; Woolley, A.T. DNA-templated construction of copper nanowires. *Nano Lett.* **3**, 359-363 (2003).
2. Stoltenberg, R.M.; Woolley, A.T. DNA-Templated Nanowire Fabrication. *Biomed. Microdevices* **6**, 105-111 (2004).
3. Becerril, H.A.; Stoltenberg, R.M.; Monson, C.F.; Woolley, A.T. Ionic Surface Masking for Low Background in Single- and Double-Stranded DNA-Templated Silver and Copper Nanorods. *J. Mater. Chem.* **14**, 611-616 (2004).
4. Becerril, H.A.; Nelson, A.R.; Woolley, A.T. Micromachined Substrates for Molecular Follow-Up in DNA-Templated Nanofabrication. *AIP Conf. Proc.* **725**, 31-40 (2004).
5. Xin, H.; Woolley, A.T. DNA-Templated Nanotube Localization. *J. Am. Chem. Soc.* **125**, 8710-8711 (2003).
6. Xin, H.; Woolley, A.T. Directional Orientation of Carbon Nanotubes on Surfaces using a Gas Flow Cell. *Nano Lett.* **4**, 1481-1484 (2004).
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8. Becerril, H.A.; Stoltenberg, R.M.; Wheeler, D.R.; Davis, R.C.; Harb, J.N.; Woolley, A.T. DNA-Templated Three-Branched Nanostructures for Nanoelectronic Devices. *J. Am. Chem. Soc.* **127**, 2828-2829 (2005).